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ONE-COMPONENT POLYURETHANE STOVING  
COATING COMPOSITIONS AND THEIR USE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to one-component polyurethane  
10 stoving coating compositions containing polyisocyanate crosslinking  
agents blocked with CH-acidic esters, especially malonic acid esters, and  
to their use for coating plastic parts.

Description of the Prior Art

The blocking of polyisocyanates with CH-acidic esters, especially  
15 malonic acid esters is known and described by the following publications:  
Petersen, Liebig's Ann. Chem. 562, (1949) 205, DE-A 30 010 60.

Using polyisocyanates blocked with malonic esters, and polymeric  
OH components (polyesters, polyacrylates, etc.), it is possible to prepare  
storage-stable "one-component coating compositions". After application,  
20 the coating compositions cure under stoving conditions of 30 minutes at  
100°C. With other isocyanate-blocking agents, for example  
butanoneoxime, 1,2,4-triazole, diisopropylamine or 3,5-dimethylpyrazole,  
such a low stoving temperature is not achievable.

However, a low stoving temperature is necessary when  
25 thermoplastic plastics, for example motor vehicle parts such as bumpers,  
hub caps or trims, are to be coated. Recently, the challenge has been to  
coat polypropylene parts with a one-component coating composition,  
which requires stoving temperature of less than 100°C.

It is known to process one-component polyurethane stoving  
30 lacquers with the conventional blocking agents mentioned above with, for  
example, dibutyltin dilaurate (DBTL) catalysts (e.g. in Farbe&Lack 7/96,  
102nd year, pages 51-58, Vincentz Verlag/Hanover).

Catalysis of one-component stoving lacquers containing  
polyisocyanates blocked with malonic esters was previously not known.

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Accordingly, an object of the present invention is to cure one-component polyurethane stoving lacquers based on polyisocyanates blocked with CH-acidic esters at stoving temperatures of < 100°C.

- It has been possible to achieve that object using the one-
- 5 component polyurethane stoving lacquers according to the invention, which contain titanium compounds as catalysts.

#### SUMMARY OF THE INVENTION

The present invention relates to aqueous- or solvent-based, one-component, polyurethane stoving coating compositions containing

- 10 i) polyisocyanates blocked with CH-acidic esters, especially malonic esters,
- ii) OH-containing polymeric compounds, and
- iii) 0.5 to 4.0 wt.%, based on the solids content of components i) and ii), of tetravalent titanium compounds.

#### DETAILED DESCRIPTION OF THE INVENTION

- 15 Fundamental to the invention is the presence of a tetravalent organic titanium compound as catalyst, which imparts to a one-component polyurethane coating composition mixture containing polyisocyanates blocked with CH-acidic esters and organic polyhydroxyl compounds
- 20 sufficiently good crosslinking even at a stoving temperature of 90°C/30 minutes. A stoving temperature of 85°C/30 minutes is also achievable.

- The titanium(IV) catalysts to be used according to the invention are mixed with the coating composition binder components, which are present in dissolved form. Those one-component polyurethane binders are stable
- 25 to storage and can be formulated, for example, as finished products for the following coating applications: filler or primer, metal base coatings, clear coatings, pigmented finishing coatings and water-reducible soft feel coatings. They may optionally contain known additives, such as pigments and flow auxiliaries.

- 30 Suitable titanium(IV) catalysts to be used according to the invention include tetra-n-butyl orthotitanate, tetraethyl titanate, tetramethyl titanate, titanium tetra-(2-ethylhexanoate), titanium triisopropylate chloride,

cyclopentadienyltitanium trichloride and mixtures thereof. Tetra-n-butyl titanate is preferred.

The titanium(IV) catalysts are used in amounts of 0.5 to 4.0 wt.%, preferably 1.5 to 2.5 wt.%, based on the solids content of binder

5 components i) and ii).

The one-component polyurethane stoving lacquers according to the invention can be used for coating a variety of substrates, for example, metals, glass, minerals, ceramics, wood, paper and plastics (such as polycarbonate, polymethyl methacrylate, polyamides and polypropylene).

10 In the following examples the invention is illustrated by means of a catalyzed clear coating composition in comparison with other catalysts based on bismuth, tin and zirconium. It is shown that the complete curing of the non-catalyzed coating composition at 100°C can be lowered by the use of tetrabutyl titanate to at least 90°C and may even tend towards  
15 85°C. The coating of polypropylene plastics parts with these one-component coating compositions would thus also appear achievable.

EXAMPLES

Starting component

Example 1

Preparation and characterization of the components of the clear  
5 coating compositions

a) Polyisocyanate crosslinking agent blocked with malonic esters

<u>Ingredients:</u>	[g]	[gram equivalents]
Desmodur W, trimerized, 80% in butyl diglycol acetate (BDGA), NCO content found: 17.1% <sup>1)</sup>	246.0	1.0
Diethyl malonate (DEM)	160.0	1.0
Na methoxide solution, 30% in MeOH	3.5	-
3,5,5-Trimethyl-3-aminomethyl- cyclohexylamine (IPDA)	8.5	0.1
Paraformaldehyde (Pafo)	3.0	0.1
Tinuvin 770 DF <sup>2)</sup>	3.7	-
Isobutanol (IB)	78.9	-
N-Methylpyrrolidone (NMP)	78.9	-
Dibutyl phosphate (DBP)	11.0	-
Blocked NCO groups	593.5	1.0
Solids, calc.:	approx. 65%	
Viscosity at 23°C:	approx. 7000 mPas	
pH:	6.3	
clear solution, Hazen color value:	approx. 50 Apha	
1 gram equivalent of blocked NCO groups:	594.0 g	

- 1) Trimerization: Desmodur W was placed in a vessel and heated to 80°C, with stirring, while a fine stream of N<sub>2</sub> was passed through. The reaction was started by addition of 3-5 ml of a 5% benzyl trimethyl ammonium hydroxide solution (in n-butanol/NMP). Additional catalyst was added in each case as soon as the reaction temperature fell below 85-90°C until the original NCO content of 32.06% fell to approximately 21.0%, corresponding to the conversion of 35% of the NCO groups present. The mixture was diluted with BDGA and allowed to cool. The pale-yellow-colored solution of trimerized Desmodur W had an NCO content of 17.1%, corresponding to an NCO equivalent weight of 246 g.
- 2) from Ciba Specialty Chemicals Inc., CH-4002 Basle

15 Implementation:

DEM and a 3.0 g portion of Na methoxide solution were placed in a vessel at 50°C with stirring. The above-described Desmodur W trimerization product was added thereto in portions. After the addition, the temperature was raised to 70-75°C and stirring was continued for approximately 5 hours until the NCO content had fallen to approximately 0.5%. The mixture was then diluted with NMP and the NCO groups that remain were reacted with IPDA.

The clear solution of Pafo, 0.3 g of Na methoxide solution and IB (half the amount) were added to the reaction solution, which was at a temperature of approximately 50°C, and stirring was carried out for 2 hours at 50°C.

The solution of Tinuvin 770 DF, DBP and IB (remainder) was then added, and stirring was carried out for approximately 2 hours at 50°C.

A storage-stable solution of a polyisocyanate blocked with malonic esters was obtained which had the properties previously mentioned.

- b) The reactant used for the above crosslinking agent blocked with malonic esters was an OH-containing polyacrylate (Desmophen A

665, available from Bayer AG, 3% OH content, OH equivalent of the solution - 567 g, 65% in butyl acetate/xylene 3:1).

### Example 2 (according to the invention)

- Preparation of a clear coating composition and curing under the influence of various catalysts

a)	Composition of the clear coating composition	
		[parts by weight]
	Crosslinking agent according to Example 1a	32.7 (0.055 gram equivalents of blocked NCO)
	Desmophen A 665 (see 1b)	31.2 (0.055 gram equivalents of OH)
	Baysilone OL 17, 10% in xylene <sup>1)</sup>	0.4
	Tinuvin 1130, 10% in xylene <sup>2)</sup>	4.1
	Tinuvin 292, 10% in xylene <sup>2)</sup>	4.1
	Butyl acetate, 1-methoxy-2-propyl acetate (MPA)	27.5
	Clear coating composition	100.0

<sup>1)</sup> obtainable from Bayer AG, 51368 Leverkusen

<sup>2)</sup> obtainable from Ciba Specialty Chemicals Inc., CH-4002 Basle

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For the purposes of the further testing, the clear coating composition was mixed with the catalyst in an amount of 1% and 2%, based on the solids content of the binder, i.e. 0.41 g and 0.82 g, respectively, per 100 g of clear coating composition. 120  $\mu$ m wet films

- 15 were produced by means of a doctor blade and stoved in an oven under the following conditions.

### Example 3 (according to the invention)

Coating of a motor vehicle mirror casing.

An uncoated mirror casing from Audi (material ABS) was cleaned using commercially available washing solutions and then rinsed with demineralized water and dried. The coating compositions listed below were applied by means of spray application using a spray gun from Sata.

- 5 The nozzle diameter was 1.4 mm and a spray pressure of 2.5 bar was used.

1. Filler application

- A commercially available two-component polyurethane filler from Du Pont (Wuppertal) was applied uniformly in a film thickness of 30 to 10  $\mu\text{m}$  and was then dried for 30 minutes at 80°C.

2. Base coat composition application

A color- and effect-providing coating composition (metallic base coat, silver, also from Du Pont) was then applied in a film thickness of 12 to 15  $\mu\text{m}$  and was dried for 5 minutes at 80°C.

- 15 3. Clear coating composition application

As the third and final coating, a clear coating composition, as described in Example 2, having the following composition was applied:

	<u>Parts by weight</u>
Crosslinking agent according to	32.7
Example 1a	
Desmophen A 665 (see Example 1b)	31.2
Baysilone OL 17, 10% in xylene	0.4
Tinuvin 1130, 10% in xylene	4.1
Tinuvin 292, 10% in xylene	4.1
Butyl acetate/MPA 1:1	26.7
Tetra-n-butyl orthotitanate	0.8
	<hr/> 100.0

- The clear coating composition was applied in a film thickness of from 40 to 50  $\mu\text{m}$  and then dried for 30 minutes at 80°C. Clear, high-gloss film surfaces with good curing and good coating properties were obtained.
- 20 b) Catalyst screening

The curing of the clear coating compositions was tested by means of pendulum hardness (DIN 53 157) and solvent resistance (which was conducted in accordance with automotive industry standards). In that method, drops of various solvents were applied in succession to the coating using cotton wool. After being allowed to act for 1 minute, the solvent was wiped off and the film was evaluated. A rating of 0 means that the coating was not damaged. In the case of the poorest score of 5, the film became detached from the substrate. Yellowing of the film was measured by means of the CieLab method. b values of approximately 1.0 were regarded as being still acceptable.  $\Delta b$  values arise when an already stoved coating composition film was over-stoved, and they must not exceed 1.0.

8 clear coating compositions were tested with the following catalysts:

1. no catalyst
2. bismuth (2-ethylhexanoate)<sub>3</sub> from King Industries
3. tetra-n-butyl orthotitanate (TBT)
4. dibutyltin dilaurate (DBTL)
5. Zr (2-ethylhexanoate)<sub>4</sub>
6. Ti (2-ethylhexanoate)<sub>4</sub>
7. Ti triisopropylate chloride
8. cyclopentadienyltitanium trichloride

As shown in the following table, tetrabutyl titanate (TBT) was the only one of the tested catalysts to begin to act even during the 80°C/30 minutes curing. With the use of 2% TBT, both the film hardness and the solvent resistance were better than the zero value. That trend becomes marked in the case of the 90°C/30 minutes curing. The solvent resistance, with a rating of 0025 with good hardness of the coating of 188 s, indicates usably good crosslinking, which was not achieved either with the zero value or with the films catalyzed with other catalysts. Furthermore, the



90°C/30 minutes curing shows that the tetravalent titanium catalysts have an advantage over the other catalysts.

- The relatively high yellowing values for titanium(IV) catalysts under over-stoving conditions at 160°C/30 minutes with  $\Delta b = 2.5-3.1$  must be
- 5 qualified to the effect that plastics do not withstand that temperature without deformation.

Catalyst study for the clear coatings

Catalyst type	1.	2.	3.	4.	5.	6.	7.	8.							
	with- out	(comparison) K-Kat 348 <sup>1)</sup> bismuth (2-ethyl- hexanoate) <sub>3</sub>	(acc. to inv.)	(comparison) Dibutyltin dilurate (DBTL)	(comparison) Zirconium 2-ethyl- hexanoate) <sub>4</sub>	(comparison) Ti (2-ethyl- hexanoate) <sub>4</sub>	(comparison) Ti triso- propylate chloride	Cyclopenta- dienyl- titanium trichloride							
Catalyst amount (calculated solid on solid)		1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%							
DRYING															
30 min./80°C															
Pendulum hardness (s.)	99	71	32	101	144	87	110	92	108	113	97	92	78	95	104
Solvent resistance															
Duration of action 1 min.															
Xylene/MPA/ethyl acetate/acetone	5555	5555	4455	5555	4455	5555	5555	5555	5555	5555	5555	5555	5555	5555	5555
0=good, 5=poor															
Yellowing (b value)	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.7	0.6	0.9	1.0	1.3	2.2	1.4	3.0

Catalyst type		1.	2.	3.	4.	5.	6.	7.	8.
	without	(comparison) K-Kat 348 <sup>1)</sup> <u>bismuth (2-</u> ethyl- hexanoate) <sub>3</sub>	(acc. to inv.) Tetra-n-butyl orthoitanate (TBT)	(comparison) Dibutyltin dilurate (DBTL)	(comparison) Zirconium 2- ethyl- hexanoate) <sub>4</sub>	(comparison) Ti (2-ethyl- hexanoate) <sub>4</sub>	Ti triso- propylate chloride	Cyclopenta- dienyl- titanium trichloride	
		1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	
Catalyst amount (calculated solid on solid) <u>DRYING</u> 30 min./90°C Pendulum hardness (s.) Solvent resistance Duration of action 1 min. Xylene/MPA/ethyl acetate/acetone 0=good, 5=poor Yellowing (b value)									
	195	150 90	161 188	160 171	153 193	199 179	192 174	186 192	
	3355	2255 2245	3345 0025	3455 2345	2345 2345	2345 1245	2345 1245	3355 2345	
	0.6 0.6	0.6 0.6	0.6 0.6	0.6 0.6	0.6 0.6	1.0 1.0	1.4 2.5	1.7 3.3	

Catalyst type	1.	2.	3.	4.	5.	6.	7.	8.
	with- out	(comparison) K-Kat 348 <sup>1)</sup> bismuth (2-ethyl- hexanoate) <sub>3</sub>	(acc. to inv.) Tetra-n-butyl orthotitanate (TBT)	(comparison) Dibutyltin dilurate (DBTL)	(comparison) Zirconium 2-ethyl- hexanoate) <sub>4</sub>	(comparison) Ti (2-ethyl- hexanoate) <sub>4</sub>	Ti triiso- propylate chloride	Cyclopenta- dienyl- titanium trichloride
Catalyst amount (calculated solid on solid)  DRYING		1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%	1% 2%
30 min./100°C								
Pendulum hardness (s.)	206	188 147	195 202	180	211	211	211	188 211
Solvent resistance								
Duration of action 1 min.								
Xylene/MPA/ethyl acetate/acetone	0014	0025 0024	0024 0002	0124 0013	0012 0012	0012 0002	0002 0012	0013 0012
0=good, 5=poor								
Yellowing (b value)	0.6 0.6	0.6 0.6	1.1 1.8	0.6 0.6	0.6 0.6	1.0 1.1	1.5 2.9	1.9 3.1
Yellowing 30 min. 100°C	0.1 0.1	0.1 0.1	2.5 3.1	0.2 0.3	0.4 0.2	1.3 2.4	2.2 3.7	1.2 1.8
+ 30 min. 160°C (Δb value)								

1) King Industries Specialty Chemicals, Kattensingel 7, 2801 Gouda, Holland

Although the invention has been described in detail in the foregoing for the purpose of illustration, it was to be understood that such detail was solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

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